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GENERATION OF A SYSTEM WHICH EXIBITS AN ISOPYCNIC IN THE CONVERSION OF ARMY VEHICLES TO SILICONE BRAKE FLUID (1)

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The US Army has been using three different automotive hydraulic brake fluids covered by Federal Specification VV-B-680, for use in all Tank-Automotive equipment (temperate -tropical areas), Military Specification MIL-H 13910 for arctic use, and Military Specification MIL-P-46046 for preservative use (2). These polyglycol and castor oil type fluids are hygroscopic and absorb water while in use which adversely affects their performance by lowering the vapor lock temperature, increasing the low temperature viscosity, and by contributing to component corrosion which can lead to cup scoring, as well as system failure.

In 1967 the US Army began developing a single multipurpose silicone based brake fluid which would overcome the absorption of water exhibited by the conventional fluids as well as provide all weather and preservative properties. This one fluids, which replaces the three existing fluids, can reduce logistics and maintanence costs. Any vehicle equipped with this fluid will be ready for use in any geographical area at a moments notice. Therefore, vehicles could be moved from the tropics to the arctic or could be put into storage without requiring any other current brake system maintanence procedures (3).

Brake Fluid, Silicone (BFS), Military Specification MIL-B-46176, which was developed by MERADCOM (4) in conjunction with industry was approved for Army use in 1980. All tactical vehicles, administrative use vehicles, commercially procured vehicles, construction equipment and material handling equipment which currently use polyglycol type fluids will be converted to silicone brake fluid by July 1982.

The wipe and clean procedure for conversion, which was successfully tested at Yuma Proving Grounds, Arctic Field Test Center, Panama Tropic Test Center (5) and was the recommended conversion method, was found to be unacceptable due to the labor intensiveness of the procedure, its implications to manpower requirements and cost. An alternate method (6) for brake fluid replacement, the flush and fill procedure (adapted for TB43-

0002-87) was approved for use based on these same considerations. A straight flush and fill procedure was tested by MERADCOM (7) and found to be inefficient for the following interdependent reasons:

a. The geometry of the wheel cylinders (bleeder valves at the top).
b. The immiscibility of the two types of fluid.
c. The lower density of the silicone relative to the polyglycol.

Figure 1 shows a cross-section of each of the wheel cylinder types and a caliper. The inlet lines and bleeder valves are indicated. The bleeder valves are always positioned at the uppermost point of the wheel cylinder to allow the lower density air to be bled from the system.

The results of testing of straight flush/fill procedure indicated that for the M-151 (jeep) vehicles, the procedure removed essentially all of the polyglycol. However, the other wheel cylinders (and calipers) do not have inlet lines located at the bottom of the cylinder and the method leaves residual polyglycol trapped in the system. Since inlet lines are in the middle of the cylinder, the fluid simply overlayers the polyglycol after removing the accessible polyglycol by displacement.

An ILIR project was initiated at MERADCOM to address this problem experimentally and to subsequently develop a cost-effective method which would achieve complete polyglycol removal.

Approach

Since the straight flush/fill method gave a liquid binary phase system (silicone polyglycol) a solution approach was used to reverse the phase structure by the inclusion of an intermediate fluid of sufficiently low density. To achieve a reversal of the phases, a fluid must be selected for which the ternary system will exibit an isopycnic tie line (8). The isopycnic tie line (or twin density tie line as it is called in multi-component systems) is that tie line at which the densities of the two phases are equal (a zero density difference). Upon passing the isopycnic line the density difference for the two phase undergoes a sign change (plus to minus or visa versa) and the phases are reversed, the upper becoming the lower and the lower becoming the upper.

The approach was, then to select a fluid which would generate an isopycnic in the silicone-polyglycol system with as high a phase boundary as possible (so that two phases will form under the various conditions found in the different wheel cylinders and calipers). This intermediate fluid must also be a cosolvent for the silicones and the polyglycols, have a high boiling point, be non-corrosive, non-hygroscopic, non-toxic, non-flammable, be inexpensive, and must be compatible with the elastomers in brake systems.

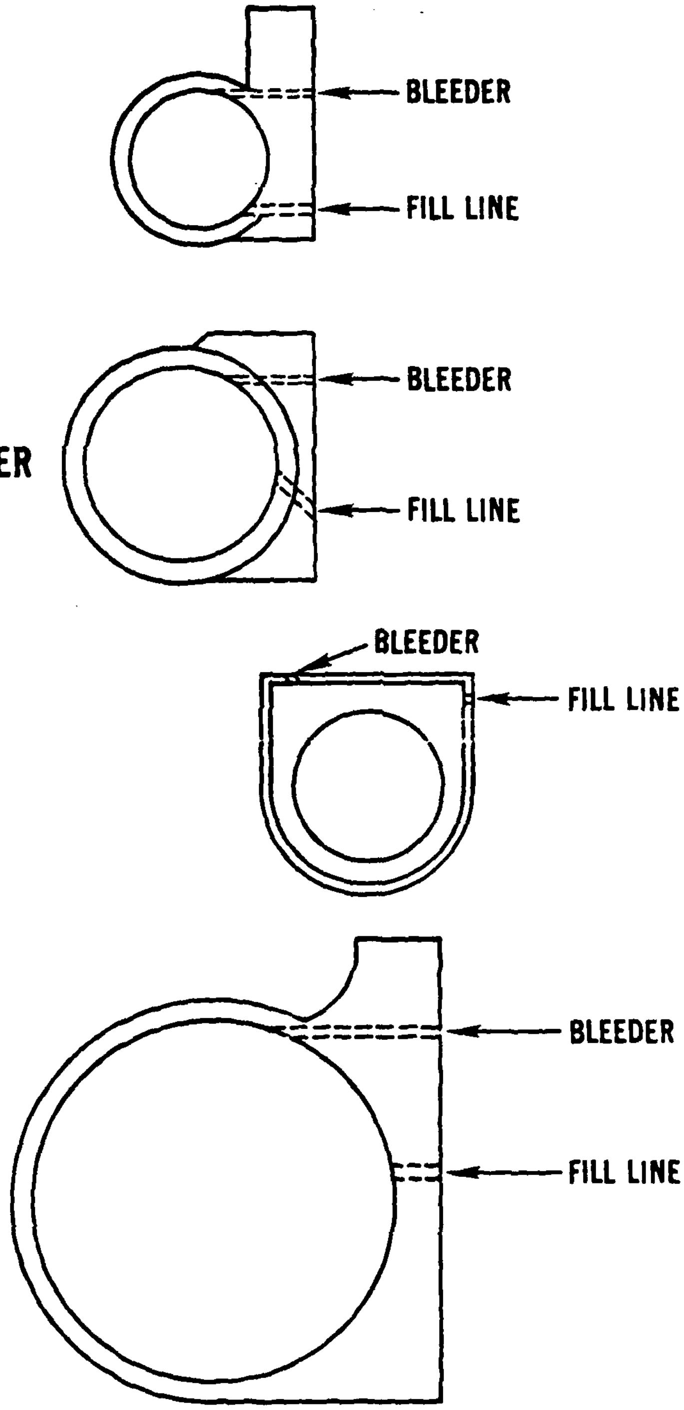
M-151 WHEEL CYLINDER
BLEEDER
FILL LINE
M-880 REAR WHEEL CYLINDER
BLEEDER
FILL LINE
M-880 FRONT DISC CALIPER
BLEEDER
FILL LINE
M-812 WHEEL CYLINDER
BLEEDER
FILL LINE

Figure 1.

Description of Tests

Air Flushing.

a. Apparatus. A wheel cylinder from a 5 ton truck with a spring, cups, and pistons was mounted in a vise and copper tubing was connected from the inlet to a syringe which had a three way valve attached to it. The syringe allowed filling of the wheel cylinder from a reservoir. A vent tube was attached to the bleeder valve of the wheel cylinder and directed to the drain.

b. Experimental. This system was used to assess the utility of air flushing for polyglycol removal. Water was used initially to check for leaks in the system.

Solvent Addition.

a. Experimental. A solvent (Table 1) known to be miscible (9) with silicones was selected (2-ethyl hexanol, 2-EH) and 1 ml was added to 1 ml of a polyglycol brake fluid. The two were miscible. To this mixture was added 1 ml of BFS. The BFS went to the bottom of the tube and retained its color. Upon vigorous shaking, the mixture formed an emulsion which settled in about 20 minutes into two distinct layers. The top layer was not transparent (a possible microemulsion) but after sitting overnight, it was clear. Gas chromatographic analysis of the layers revealed that the bulk of the polyglycol and the 2-EH were in the yellowish upper phase, and that a small portion was in the lower clear phase (the dye from the BFS went into the polyglycol layer). The 2-EH was then tested and found to be a solvent for BFS (Figure 2).

Wheel Cylinders And Plexiglass Windows.

a. Apparatus. For the purpose of visually observing the mixing, a wheel cylinder from a 5 ton truck was equipped with end plates made of plexiglass and bolted into place to provide a fluid seal. The spring, pistons and cups were removed for viewing, and the dust boots were trimmed so that the window diameter was approximately 1-½ inches for easy viewing of the process. A lamp was placed at the rear of the assembly so that the interior of the cylinder was illuminated.

b. Experiments. The wheel cylinder was charged with polyglycol and a series of experiments was performed for the purpose of determining the feasibility of the method and ascertaining if effective mixing could be accomplished. The degree of mixing, aeration of the fluids and phase behavior were observed visually.

Mock-Up of A Brake System.

a. Apparatus. A system of six wheel cylinders and a master cylinder was constructed, and they were connected with ¼ inch cooper tubing. The wheel cylinders were bolted to a bracket so that they could be bled properly.

b. Experiments. Systems of long and short lines were used, and

Table 1. Properties Of 2-Ethyl Hexanol (2-EH).

Molecular Weight	130.22
Boiling Point	364.6°F
Freezing Point	-104.8°F
Density(g/cm^3)	0.8323
Vapor Pressure (68°F, mbar)	0.5
Water Absorption (%)	2.7
Flash Point	178.°F
Ignition Temperature	482.°F

Table 2. Residual Polyglycol After Air Flushing.

	ml	%
Air Flush	51	37
Reverse Flush	8	9.4
Vacuum	49	57.6

Note: The volume of the wheel cylinder was 85 ml.

Table 3. Results Using Wheel Cylinders And Plexiglass Windows.

	Extent Of Mixing	Aeration Of Contents	BFS On/Top Bottom	BFS Aerated	Mixing Of BFS/Glycol
Add 2-EH By Syringe	None	-	-	-	-
Air Purge Of Glycol then Hexanol	None	Aerated Polyglycol	-	-	-
Air Purge Before And After Hexanol	Complete	Aerated Polyglycol	BFS/Top Aerated Glycol/ Bottom	No	None
Pressure Flushing 2-EH	Incomplete At Bottom	-	-	-	-

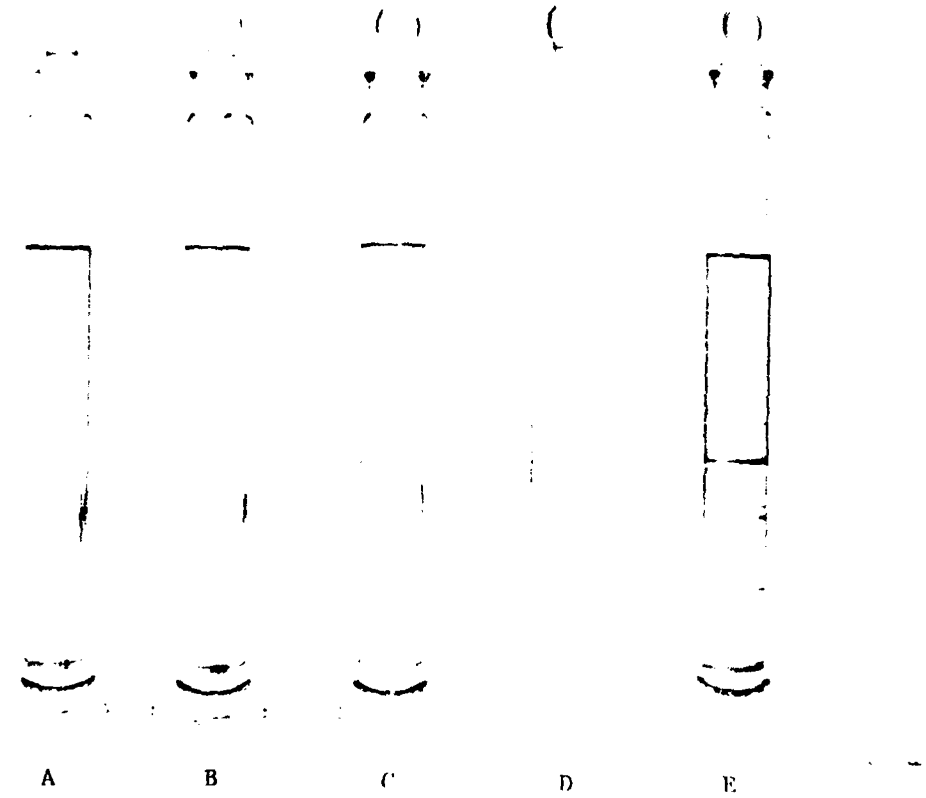

Figure 2. The Phase Inversion Phenomenon. A= polyglycol fluid; B= silicone fluid; C= after addition of silicone to polyglycol, silicone on top; D= 2-ethyl hexanol (2-EH); E= after mixing polyglycol and 2-EH and then adding silicone, silicone on the bottom.

different flushing volumes of the density modifier were used to develop a method for eventual use in the conversion of vehicles.

Caliper Experiments.

a. Apparatus. A caliper from a commercial vehicle was attached to the master cylinder with a three foot line, and spacers were clamped into the caliper to fix the internal volume at 90 ml.

Used Wheel Cylinder.

a. Apparatus. A used wheel cylinder from a 5 ton truck was connected to the master cylinder, and flushing experiments were conducted to determine the effect of the sludge and the extent of sludge removal for this process.

Administrative Vehicle Test.

a. Apparatus. This vehicle was selected because it had wheel cylinders and calipers, and because it had over 100,000 miles on it so it could be expected to be a worst case test.

b. Test. A proposed procedure based on previous experiments was used and the vehicle converted. This procedure involved purging the system with air, flushing the two rear wheel cylinders simultaneously and then flushing with the 2-EH. The wheel cylinders were flushed with one volume of the master cylinder (200 ml) and the calipers were flushed individually with twice this amount of fluid. After the fluid flushes, the air (used for flushing) was allowed to purge the system for one minute after the fluid was purged. The vehicle was then pressure bled with BFS while allowing a specific volume of the BFS to pass through the system to insure complete removal of the 2-EH. The wheel cylinders and calipers were removed for analysis and subsequently replaced.

Demonstration Of The Method.

a. Apparatus. This demonstration of the method for TACOM involved the conversion of a 2-½ ton vehicle and a jeep. A second 2-½ ton vehicle was converted on a trial run basis prior to the demonstration. An M-880 and a 5 ton truck were available for this demonstration but were not converted.

Phase Diagram For The BFS/Polyglycol/2-EH.

a. Apparatus. This diagram was prepared by the titration method, using the fully formulated brake fluids (10).

Infrared Examination Of Hydrogen Bonding Effects.

a. The instrument used for the infrared examination of hydrogen bonding effects in these fluids was a Perkin Elmer 580 using various cells.

<u>Results Of Tests</u>

Air Flushing. The results using three flushing techniques are given in Table 2. With air flushing and vacuum suction (at the bleeder), the residual polyglycol levels are high.

Solvent Addition. This experiment demonstrated the density inversion process. The 2-EH, being a density modifier, reduces the density of the polyglycol to such an extent and in such a manner that upon addition of the silicone, two layers form with the silicone on the bottom. This phenomenon provides the basis for effective polyglycol replacement, the mechanism of which is displacement as opposed to dilution. A critical element in this approach is to achieve complete mixing of the density modifier with the polyglycol fluid especially at the lower part of the wheel cylinders (and calipers).

Wheel Cylinder And Plexiglass Windows. The results of these experiments are outlined in Table 3. The air flushing method for mixing was found to be effective in this system. These experiments established the feasibility of the method and determined that air purging was the method of choice for mixing the density modifier with the polyglycol.

Mock-Up Of A Brake System. The results of these tests are given in Table 4 and a simultaneous flushing technique was found to be feasible in the mock-up.

Caliper Experiments. These experiments demonstrated that a single flush was not sufficient for calipers.

Used Wheel Cylinder. A used wheel cylinder from a 5 ton truck was flushed with 400 ml of 2-EH and emptied into a flask. After the addition of BFS (500 ml), the upper layer contained the particles of sludge broken loose by the flushing. After shaking, a single layer formed and the sludge, to some extent, appeared to have broken up the two phase system when agitated.

Conversion Of An Administrative Vehicle. Table 5 lists the results of the analysis of the fluid from each wheel cylinder and caliper as well as the fluid used. Clearly the method was found to be an effective method for the replacement of polyglycol brake fluid by silicone brake fluid.

Demonstration Of The Method. The results of the analysis of the fluid from the 2-½ ton vehicle used in the dry run of the method are shown in Table 6. Sludge from the walls of the driver side front wheel cylinder did break loose and drained out of the cylinder during disassembly. The observation of a measurable amount of glycol in one of the wheel cylinders is probably due to entrainment of the polyglycol fluid by the sludge, which would render it inaccessible to dissolution by the solvent.

Table 4. Results Of Mock-Up Experiments.

Experiment	Flushes	Residual Alcohol	Residual Polyglycol
Short Lines	3	-	Traces
Long Lines	3	0.96-1.49%	No Trace
Long Lines	2	1.19-6.30%	No Trace
Long Lines	1	1.47-4.29%	Traces

Note: All wheel cylinders were flushed simultaneously.

Table 5. Results Of Conversion Of An Administrative Vehicle.

Wheel	Alcohol Used	Fluid Collected	Residual Polyglycol	*VLT
PR	145 ml	250 ml	None	435°F
DR	145 ml	130 ml	None	453°F
PF	870 ml	285 ml	None	490°F
DF	580 ml	275 ml	None	480°F

Note PR= Passenger rear, etc.,*VLT= Vapor lock temperature.

Table 6. Fluid Analysis From Demonstration With A 2-½ Ton Vehicle.

Wheel Cylinder	Residual 2-EH (%)		Polyglycol
	200 ml	230 ml	
PR1	2.3	0.8	NT
PR2	0.95	0.7	2%
PF	1.6	0.6	T
DF	1.0	0.8	NT
DR1	2.5	0.9	T
DR2	1.7	0.95	T

Note: DF= Driver front, 2-EH column is the volume of BFS passed through the system after conversion, NT= No trace.

Miscellaneous Testing. Table 7 lists a summary of additional testing and evaluation of the use of 2-EH as a flush fluid.

Phase Diagram Determination. The phase diagram was determined using the titration method for the system BFS/Polyglycol/2-EH and Figure 3 shows the diagram obtained. There is a high phase boundary and a low isopycnic line. The BFS and polyglycol used were the fully formulated brake fluids. The working area is above the isopycnic and below the phase boundary. Below the isopycnic, the silicone will be the upper phase. Above the phase boundary a single phase will form (displacement by dilution). There is a slight concavity on the right side of the curve which is assumed to be the result of some additive. The majority of the possible combinations are within the working area and this provides the flexibility needed to develop a method for different vehicles using simple procedures.

Infrared Examination Of Hydrogen Bonding Effects. The -OH stretching bands in dilute solutions were examined. Table 8 lists the bands as well as the spectral shifts due to hydrogen bonding. The spectral shifts for the 2-EH in silicone is smaller than that in glycol which indicates (11) that a weaker hydrogen bond forms in the silicone and may partially explain the preference of the cosolvent for the polyglycol which generates the high phase boundary curve.

Conclusions

A method was developed which is effective at complete polyglycol removal and is illustrated on the right side of Figure 4. The method makes use of an intermediate fluid (2-ethyl hexanol, 2-EH) whose properties are such that a reversal of the phases is induced. Air is used to mix this density modifier with the polyglycol prior to adding the BFS. The method is thus based on the generation of a system which exibits an isopycnic (or twin density) tie line in the phase diagram of the multicomponent binary phase system. While the 2-EH is a solvent for both the BFS and the polyglycol, it greatly prefers the polyglycol in a ternary mixture as is evident from the height of the phase boundary curve (Figure 3). The frequency shifts of the -OH stretching bands indicate a weaker hydrogen bonding of the 2-EH with the silicone as opposed to the polyglycol or the 2-EH itself and may partially explain this preference. In addition, since this procedure does not involve and equilibrium binary phase system, the phase boundary curve may be considered to be the worst case in conducting a conversion using this method.

In addition to having other necessary properties such as a high boiling point, a low freezing point, low flammability, and low moisture absorption, the 2-EH is cost-effective, non-toxic, and is compatible with brake system elastomers in the concentrations generated by this method.

Table 7. Results Of Additional Testing.

Property	2-EH	Parameter In MIL-B-46176 (BFS) Level	2-EH Tested	Value	Result
Boiling Point	364.6°F	Vapor Lock Temp.	2%	450°F	Pass
Freezing Point	104.8°F	Pass at -65°F	-	-	Pass
Flash Point	185°F	400°F	-	-	Pass
Elastomer Compatability	-	As Stated	2%	-	Pass
Stroking Performance	-	As Stated	3%	-	Pass
Density (g/cm^3)	0.8323	-	-	-	Pass
Moisture Absorption	2.7%	Wet Vapor Lock Temperature After Humidification (0.1% water by Karl Fischer)	5%	360°F	Pass
Toxicity	Slight	-	-	-	Pass
Cost	$3.15/Gal. (bulk rate)	$15-17/Gal.	-	-	Pass

Note: The minimum flash point for VV-B-680 fluids is 179.6°F.

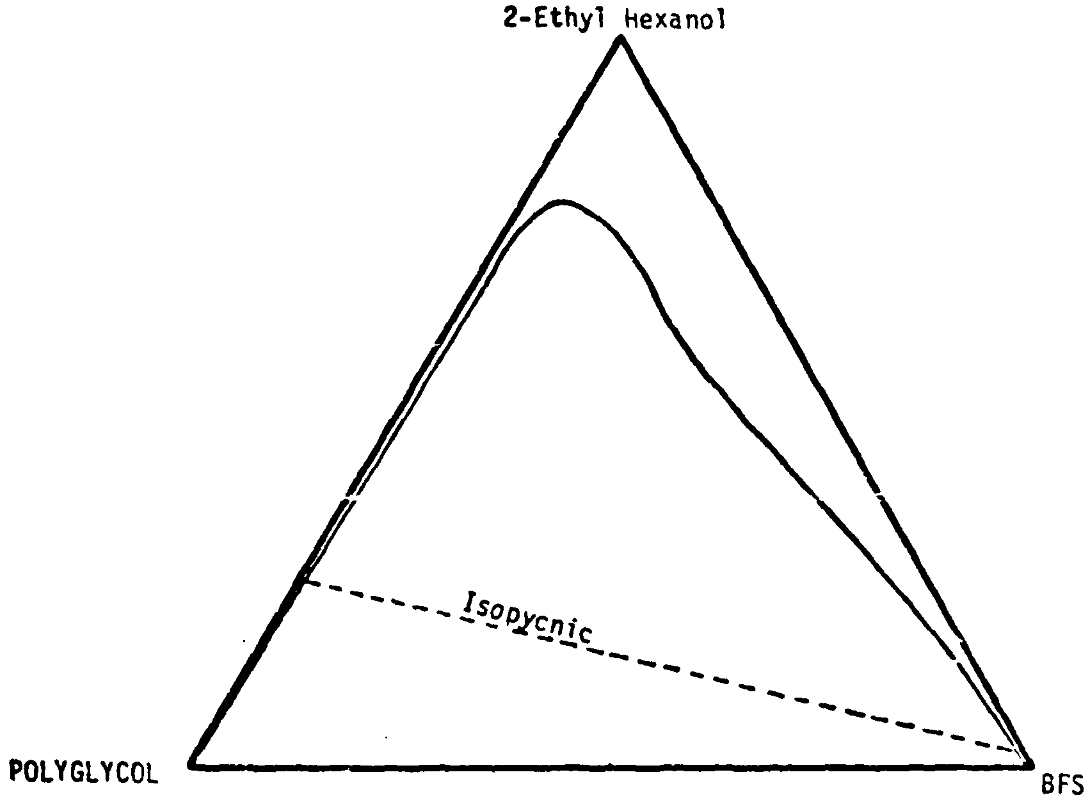

Figure 3. Phase Diagram For The BFS/Polyglycol/2-EH System. The fully formulated fluids were used. The slight concavity on the right side of the diagram is assumed to be due to additives. Note the high phase boundary and the low isopycnic (dashed line).

Table 8. Hydroxyl Stretching Frequencies For Alcohols.

Concentration (%)	Monomer	Dimer	Polymer	
2-EH/CCl_4				
2	3639	3499	3359	280
1	3639	3523	-	126
0.5	3639	3510	-	129
neat	3640	-	-	300
2-EH/BFS				
2	-	-	3400	239
10	-	-	3440	199
Cyclopentanol/CCl_4				
2	3624	3490	3357	267
1	3624	3495	3365	259
0.5	3624	3505	3365	259
neat	-	-	3340	
Cyclopentanol/BFS				
Saturated Solution	-	-	3340	284
n-Butanol/CCl_4				
2	3636	3494	3344	292
1	3636	3503	3360	276
0.5	3638	3511	-	127
neat	-	-	3340	296

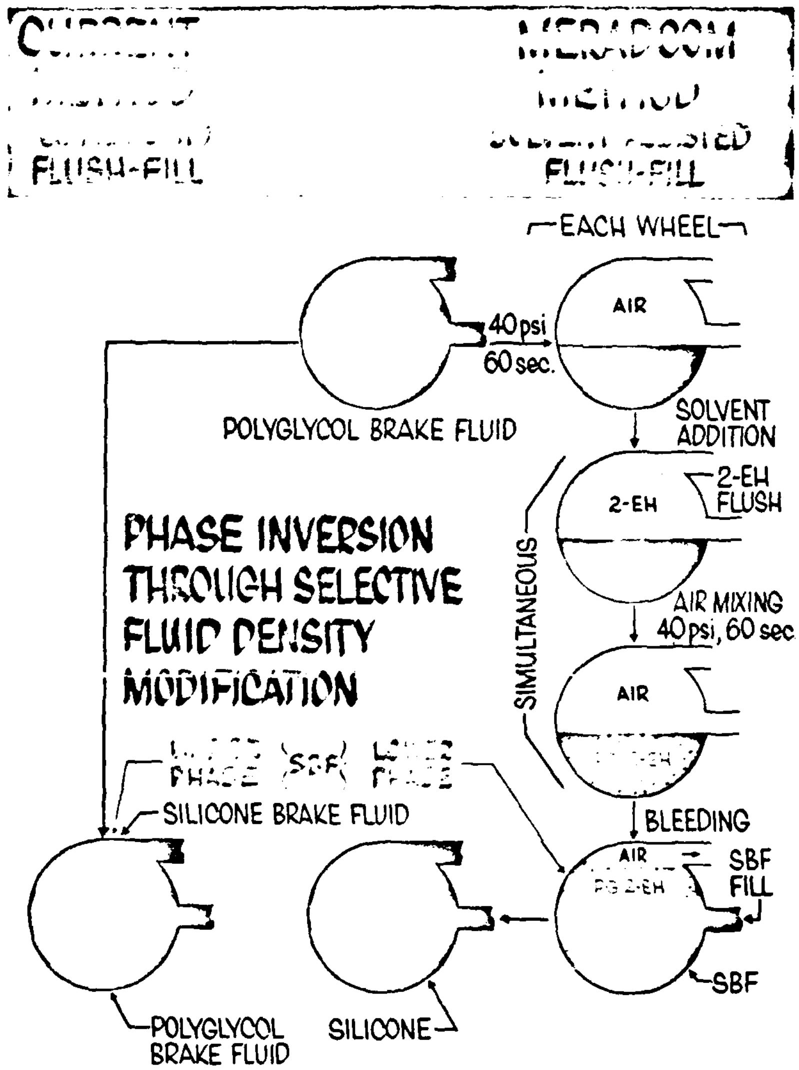

Figure 4. Comparison of Flush/Fill and Solvent Assisted Flush/Fill Procedures For The Conversion of Tank-Automotive Equipment to Brake Fluid, Silicone (BFS).

The USMC will be using the method (which is being patented) to convert their shipboard vehicles on board the Near Term Prepositioned Fleet at Diego Garcia to BFS. An extension of the method covering mineral fluid based systems is being considered by industry. The conversion to BFS is expected to save the US Army $21M over the next 10 years. This method could not only recapture the all climate utility and high vapor lock temperature of BFS but could substantially increase the cost-effectiveness of the conversion.

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